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**The Spectrophotometric Determination of Resorcinol
in Colloidal Propellants (C)**

F.I.H. Tunstall

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Gr. Brit.

Technical Note No. 10

February 1970

The Spectrophotometric Determination of Resorcinol
in Colloidal Propellants (C)

by

F.I.H. Tunstall

SUMMARY

The method for determination of resorcinol which is based on spectrophotometric measurement of copper nitrosoresorcinate has been modified to improve its sensitivity and reliability.

Resorcinols.
Double base rocket propellants.
Spectrophotometry.

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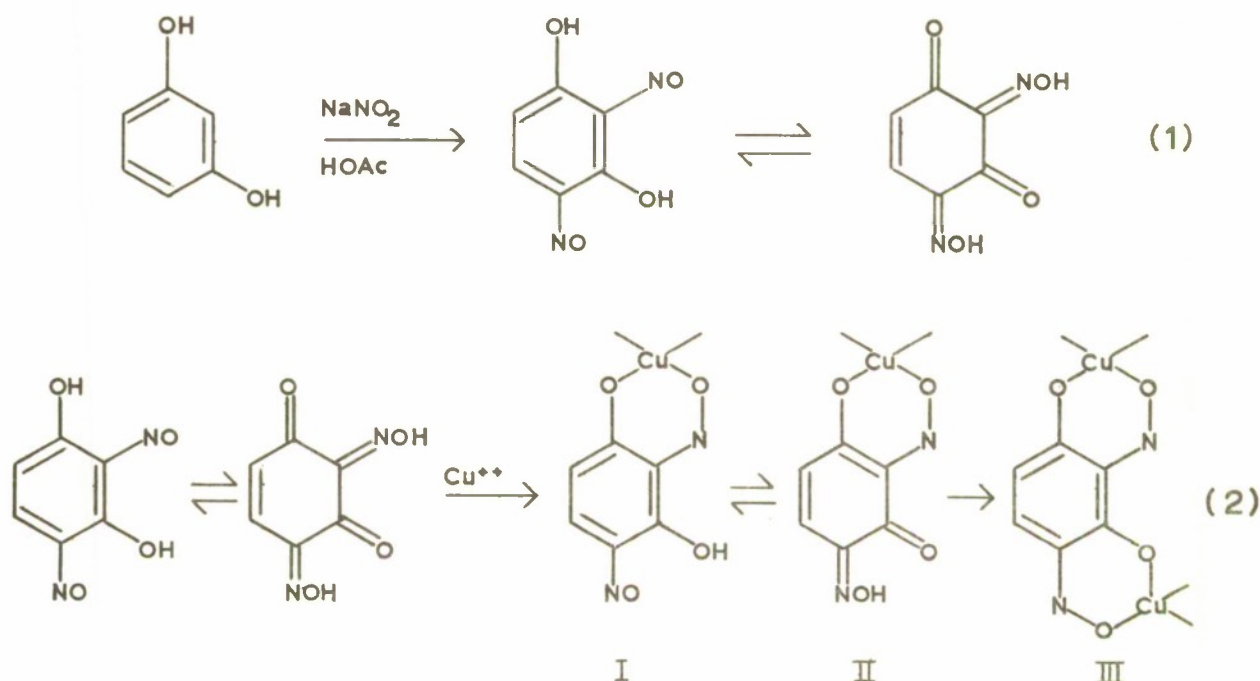
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Reference: WAC/205/08

1. INTRODUCTION

To determine resorcinol by the method given in Reference 1, the propellant is first extracted with dichloromethane. Resorcinol is then separated from other soluble ingredients including NG, triacetin, and 2-NDPA by washing with water. Treatment of the aqueous extract with sodium nitrite and dilute acetic acid produces 2:4-dinitrosoresorcinol (Eqn. 1) and addition of copper sulphate solution produces a yellow copper dinitrosoresorcinolate complex (Eqn. 2). This exhibits two absorption maxima at 290 and 340 mm and measurement at 340 mm enables resorcinol to be determined. The structure of the complex is indefinite and the reaction probably proceeds through several equilibria as follows:



The considerable water solubility of resorcinol enables it to be separated from almost all other propellant ingredients which might interfere with the estimation and the method can be used satisfactorily to analyse degraded propellants from ageing trials. Since the work was completed several authors have described chromatographic procedures for the determination of resorcinol in CMCDB propellant compositions.^{2,3,4} Propellant samples from compatibility tests which are mixed with rubber and other materials have also been analysed successfully, although in such work it is necessary to prove in each case that the method is unaffected by this contamination. It is sometimes preferable to use diethyl ether rather than dichloromethane for the preliminary extraction of these

/mixtures

mixtures in order to reduce the amount of soluble material which is extracted from the contaminant.

The only propellant ingredient which has been found to interfere with the procedure is lead β -resorcylate, which hydrolyses to produce 2:4-dihydroxybenzoic acid. This is sufficiently soluble in water to accompany resorcinol and reacts slowly with the resorcinol reagents causing somewhat high results to be obtained. Interference due to stabiliser degradation products was also considered, but this seemed unlikely in view of earlier work^{1,5} in these laboratories which showed that the principal degradation products from resorcinol are high molecular weight compounds such as resorufin and rezazurin, and related condensation products. The formation of these products depends upon initial nitrosation of resorcinol, but there is no evidence to suggest that the intermediate nitroso compounds are themselves present in aged propellant, hence there is no reason to suspect interference from this source. However, as a precautionary measure the analysis was performed in the presence of 4-nitrosoresorcinol; no interference was observed even when relatively large proportions (ca. 30% of resorcinol content) of the nitroso compound were used.

Although the original procedure proved reasonably satisfactory for normal propellant analysis, a lack of precision in the results was often observed. During studies of the reactivity of resorcinol as a stabiliser, in which it was necessary to determine with a greater accuracy rather low rates of consumption of resorcinol after heating in solution in nitroglycerine, it became evident that variations in the concentrations and quantities of the reagents which were used could have considerable effects on the results. This might be expected from the reactions leading to structure III above which would obviously be favoured by an increase in copper ion concentration.

2. EXPERIMENTAL

Variations in the quantities of reagents and their effects were studied as follows:

(a) In the original method, the methylene chloride solution obtained by extracting 1 g of propellant was washed with 3 x 20 ml of water and the resulting aqueous extract made up to 100 ml. 5 ml of this solution was mixed with 2 ml of 2% sodium nitrite solution, 20 ml of 10% acetic acid was then added, followed by 2 ml of 3% copper sulphate solution. A blank determination on the reagents was necessary to complete the estimation. It was found that the amount of sodium nitrite could be reduced to 2 ml of 0.2% solution without affecting the development of the yellow copper complex. This considerably reduced the level of the blank with a consequent improvement in the quality of the results.

(b) The absorption spectra of solutions of the copper dinitrosoresorcinate complex as obtained by the original procedure are shown in Fig. 1. By reducing the sodium nitrite concentration and increasing the amounts of copper sulphate to a maximum of 0.5 g, the absorbance at 340 mm is increased and that at 290 mm decreased as shown in Fig. 2. The change of absorbance

/against

against amount of copper sulphate added is shown in Fig. 3 and it is evident that, at the low concentration required by the original method, a considerable error could result from a minor fluctuation in the amount of reagent which was added. The data showed that the method would be improved by amending the reagent concentrations as follows:

5 ml 0.2% sodium nitrite solution and 5 ml of 10% copper sulphate solution to be used for the formation of copper nitrosoresorcinol.

The detailed procedure is given in Section 3 (iii).

3. PROCEDURE

(i) For propellants, extract an appropriate quantity of the prepared sample for 10 hours with dichloromethane in a Soxhlet extractor. Carefully distil the extract avoiding excessive heating and redissolve in about 20 ml of chloroform. If other stabilisers, e.g. 2-NDPA, are to be determined it is convenient to make the chloroform extract up to 50 ml and pipette 25 ml for the resorcinol determination into a small separating funnel. The remaining solution is then available for further analysis.

In the preparation of samples, composite modified type propellants should be cut into small thin slices not more than 1 cm² and 1 - 2 mm thick. They should not be ground, owing to possible segregation of aluminium. Ordinary double-base propellants, and similar compositions can, of course, be ground.

For other samples or extracts dissolve an appropriate quantity 20 - 25 ml chloroform in a separating funnel.

(ii) Extract the chloroform solution 5 times with 25 ml portions of water filtering the extracts through a cotton wool plug into a 250 ml graduated flask. Make the solution up to the mark with water.

(iii) Pipette a suitable aliquot to contain approx. 0.5 mg of resorcinol into a 100 ml standard flask. Add 20 ml 10% acetic acid and 5 ml 0.2% sodium nitrite solution and allow to stand for 5 minutes, then add 5 ml 10% copper sulphate solution, dilute to the mark and allow to stand for 20 minutes. Measure the optical density of the solution at 340 nm in 5 mm cells against a reagent blank prepared as above omitting the sample aliquot.

(iv) From a calibration graph prepared with pure resorcinol calculate the percentage resorcinol in the sample as follows:

$$\% \text{ Resorcinol} = \frac{M \times D}{W}$$

where M = mg resorcinol in 100 ml solution
D = dilution factor
W = sample weight, g

The current calibration graph is shown in Fig. 4.

/Calibration

Calibration graphs produced in the absence and presence of NG by the extraction procedure given in 3 (ii) were identical.

4. RESULTS

The following results, expressed as weights of resorcinol in milligrammes, are from experiments in which nitroglycerine samples weighing 2.27 grammes (0.01 moles) and containing 0.5 and 2.0 molar per cent additions of resorcinol were heated at 80°C for 24 hours. The results from these experiments were self-consistent and corresponded well with the behaviour expected from such mixtures under these conditions.

0.5% Molar

1)	4.63	4.75	2)	4.52	4.50	3)	4.88	4.90
4)	4.45	4.45	5)	4.40	4.40			

Standard deviation (equal to the square root of mean variance between pairs)

$$= \sqrt{\frac{\sum (x_1 - x_2)^2}{2n}} = 0.04 \text{ (0.85\%)}$$

2.0% Molar

1)	20.65	20.55	2)	20.30	20.30	3)	19.55	19.85
4)	19.65	19.75	5)	20.15	20.45			

SD = 0.14 (0.70%)

Typical results from compatibility testing of CMCDDB propellant are given below showing the stabiliser contents of propellant samples after heating alone and with various Hypalon rubbers. The rates of stabiliser loss from the propellant, being no greater when heated in contact with the rubbers, show their mutual compatibility.

Sample	Heating Time	Resorcinol, %		
F452/302/19	Control	1.18	1.20	1.21
	2 weeks 60°C	1.08	1.10	1.08
	4 weeks 60°C	0.96	0.96	0.96
F452/302/19 + 5% Rubber	1	"	1.02	
	2	"	1.05	
	4	"	1.05	
	7	"	1.02	
	10	"	1.03	

5. CONCLUSIONS

The revised method is applicable to the determination of resorcinol in heated mixtures with nitric esters, colloidal propellants which do not contain lead β -resorcylate, and in compatibility studies of propellant with various

/plastics

plastics, rubbers and adhesives.

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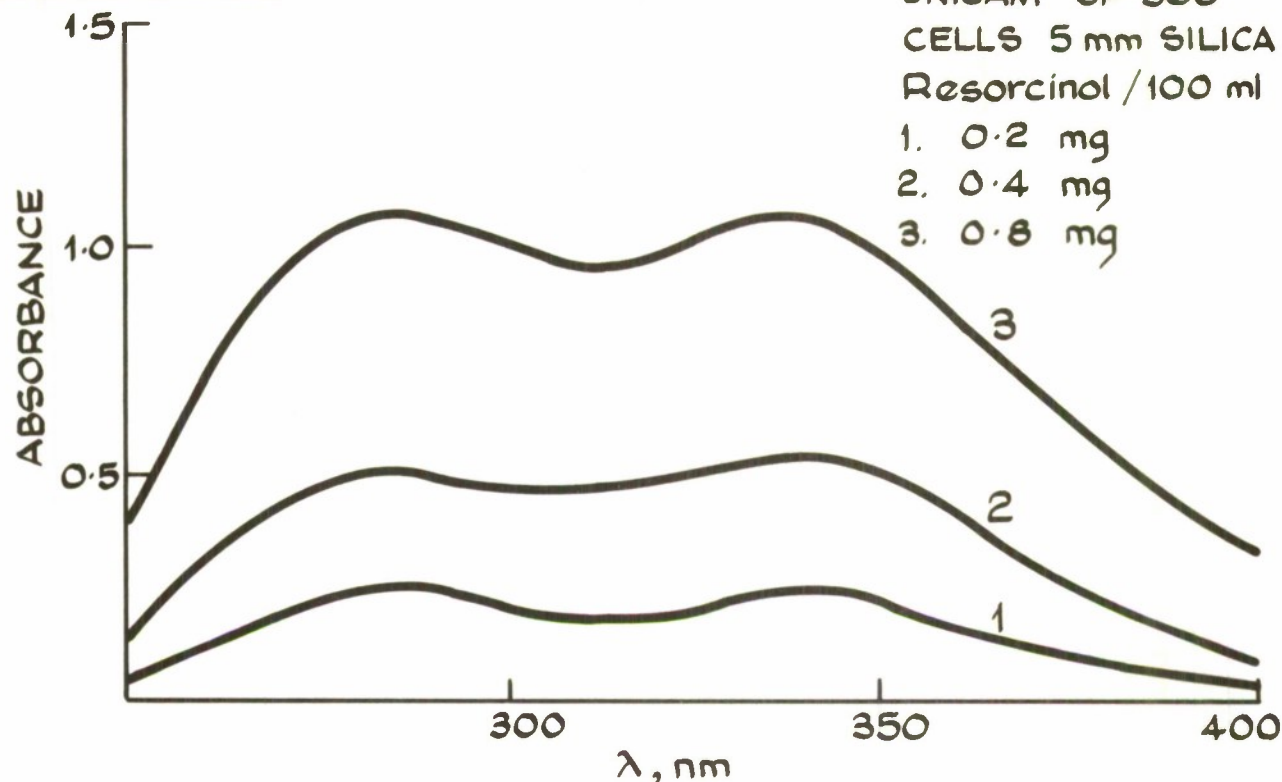


FIG.1 GRAPH OF ABSORBANCE VS WAVELENGTH
FOR COPPER DINITRORESORCINATE
SOLUTION. ORIGINAL PROCEDURE.

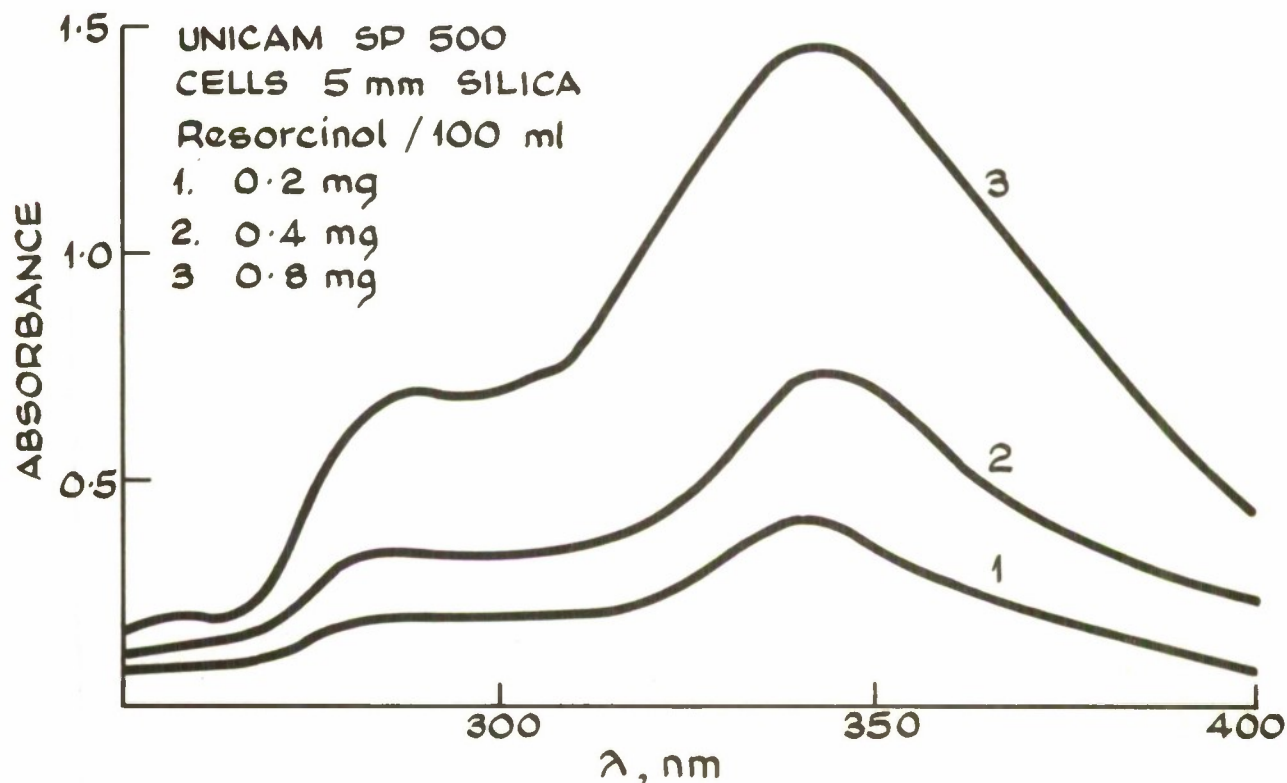


FIG.2 GRAPH OF ABSORBANCE VS WAVELENGTH
FOR COPPER DINITRORESORCINATE
SOLUTION. REVISED PROCEDURE.

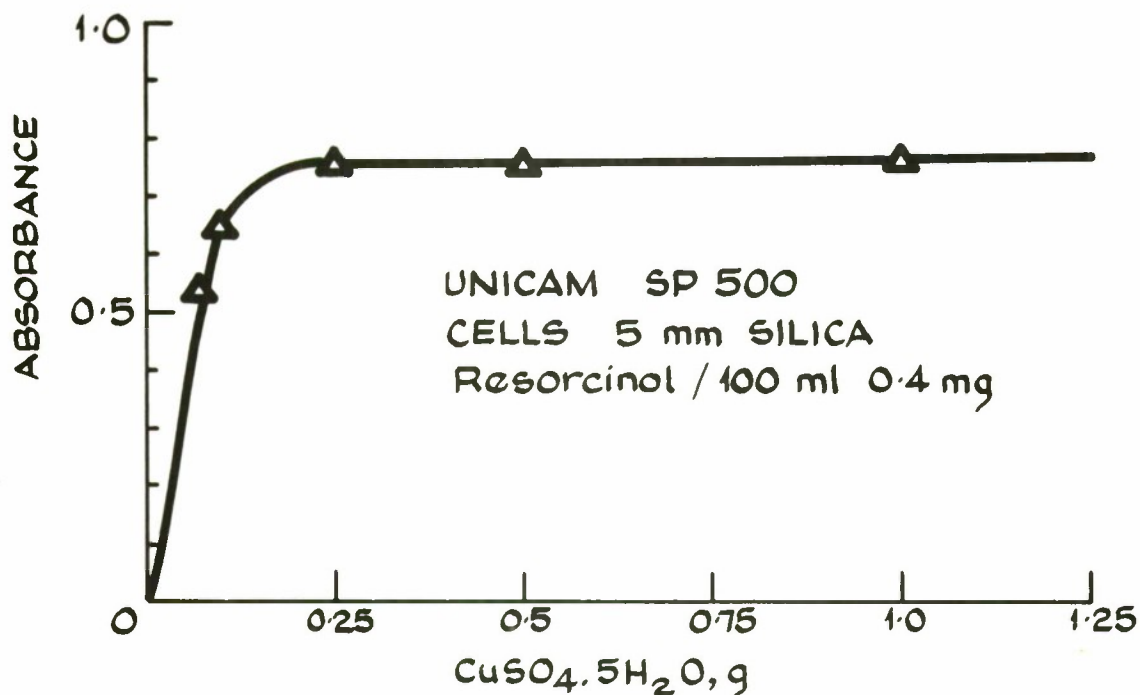


FIG.3 GRAPH OF ABSORBANCE VS AMOUNT
OF $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ADDED.

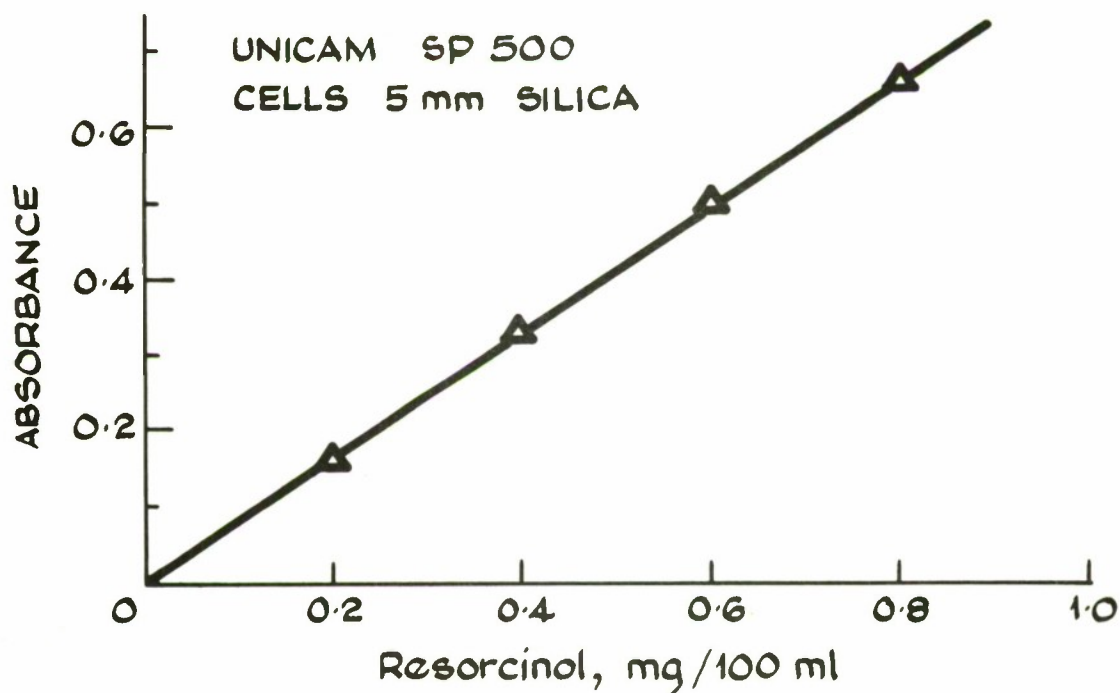


FIG.4 GRAPH OF ABSORBANCE VS CONCENTRATION
OF RESORCINOL.

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